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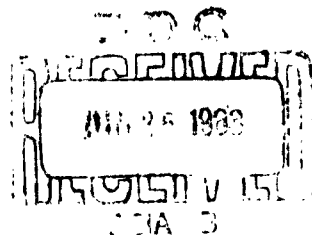# DEVELOPMENT OF A DEVICE TO OBJECTIVELY DETECT AND RECORD THE PRESENCE OF MINUTE AMOUNTS OF GASES IN THE ATMOSPHERE

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NOTICE

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FOREWORD

This report summarizes the development of an instrument to detect certain air pollutants. The work was carried out under Contract AF 30 (602)-2655. The contract was initiated under Project No. 5534, Task No. 553402. The work was administered under the direction of the Directorate of Intelligence and Electronic Warfare, Research and Technology Division, Air Force Systems Command, Griffiss Air Force Base, New York. Mr. Donald D. Dylis was the project engineer.

This report covers the work done in the period February 1962 to April 1963.
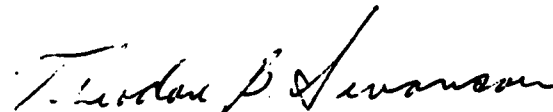
ABSTRACT

An electro-chemical sensing device has been developed for the measurement of HCl, HF, NO_2, and O_3. The instrument has a dual flame ionization detector that can also be operated as a single flame. The inorganic gases are converted to organic gases which are then detected with the flame ionization detector.

PUBLICATION REVIEW

This report has been reviewed and is approved.

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ABSTRACT

An electro-chemical sensing device has been developed for the measurement of HCl, HF, NO_2, and O_3. The instrument has a dual flame ionization detector that can also be operated as a single flame. The inorganic gases are converted to organic gases which are then detected with the flame ionization detector.

PUBLICATION REVIEW

I. INTRODUCTION

The objective of this project was to develop a specific detection system for air pollution by HCl, HF, UDMH, NO_2 and O_3 in the range of one to ten parts per million (ppm) of each of the pollutants.
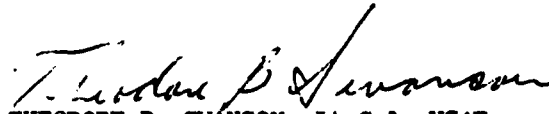
The original proposal outlined a system composed of argon, electron capture, xenon and flame ionization detectors coupled with a multi-channel magnetic recorder. After the contract work had begun, an engineering change was initiated by the sponsor excluding the use of bottled gases. This necessarily eliminated the argon, electron capture and xenon detectors.

Several possibilities of merit remained after the exclusion of bottled gases. One device that was considered was the use of radioactive compounds to be released by the pollutants and detected by conventional tracer methods. The scope of this work would require and investigation to determine the best possible reactants with the pollutants, followed by a program to synthesize the reactant materials using carbon 14 labeled compounds. It was felt, however, that due to time considerations, it would not be possible to accomplish so large a task. The alternate method would be the use of the flame ionization detector assuming that fuel could be supplied.

It was believed that a generation system for hydrogen or carbon monoxide could be devised to furnish fuel for the flame ionization detector. Flame ionization detectors do not respond to inorganic vapors, therefore, it would be necessary to convert all of the inorganic contaminants to organics. This could be done by a series of specific reaction tubes. These reaction tubes would contain organics or organo-metallics, and it was feared that bleeding from the tubes might be a problem. If a dual flame detector was used and the pollutants not allowed to react on the reference side then any bleeding by the reactant column would be compensated for.

It was decided to use a dual flame detector with a selector valve assembly so that each gas could be sampled in turn. There would be six pair of tubes and valves, one pair for each of the five pollutants and one pair for a zero base line. Each pair would consist of a sample tube and a reference tube.

This simplified the job of the recording system. It now became feasible to use a single channel recorder rather than the multi-channel one proposed earlier.

II. EXPERIMENTAL

The experimental work was divided into several separate tasks which are discussed separately.

A. Fuel System

The engineering change instituted by RADC eliminating the use of bottled gases caused a complete revision as to the possible solution of the problem. The argon, xenon, and electron capture detectors were removed from further consideration because of this limitation. There appeared to be two possible solutions using conventional chromatograph detectors, the flame ionization detector, or the thermal detector. The flame ionization detector is much more sensitive than the thermal detector so it was decided to use the flame. This, of course, created the problem of a fuel supply for the flame; however, it was believed that a fuel supply could be generated in situ for the instrument.

There were two fuels that could be used, carbon monoxide and hydrogen. The carbon monoxide could be generated in situ by the reaction of sulfuric and formic acids. Then using CO as a fuel for the flame ionization detector, the work was begun. It was found that using a piece of 1/8" stainless tubing for a burner tip the flame could be sustained with CO flow of 40 cc/min and sample flow of 25 cc/min. However, the flame was very noisy and the slightest pressure surge in the system would extinguish it. It appeared that the gas velocity was greater than the propagation rate of the flame since the flame was seen on occasion to jump up and burn on the collector electrode. It was concluded from the studies that carbon monoxide could be used if necessary but that it would be better to concentrate on a source of hydrogen since the flame ionization detector is designed for the use of hydrogen.

Hydrogen can be generated from the reaction of sodium borohydride with water if a cobalt chloride catalyst is used. Metal Hydrides, Inc. has such a compound on the market. It is in pellet form composed of 92.5% $NaBH_4$ and 7.5% $CoCl_2$ (anhydrous). One pellet 5/16 inch in diameter yields 670 cc of H_2 at STP according to the reaction:

$$4 \ CoCl_2 + 8 \ NaBH_4 + 18 \ H_2O \longrightarrow 2 \ Co_2B + 8 \ NaCl + 6 \ H_3BO_3 + 25 \ H_2 \uparrow$$

These pellets are marketed under the trade name Hydra Pills

There are two general methods of utilizing these pellets. One is to generate the hydrogen in a large high pressure vessel (1800 psig) and refill small bottles from it. The second would be to use a low pressure

generation system in the instrument itself; this would, of course, make the package larger. The further development of this fuel supply was left for a later date, since it had been shown that it is feasible to generate hydrogen chemically.

The instrument was then designed to utilize lecture bottles of hydrogen with the above in mind. A lecture bottle of hydrogen should permit operation of over ten hours.

B.   Dual Flame Detector

The flame ionization detector will respond to as little as 10^{-10} to 10^{-12} mole of solute in the carrier gas. Its operation is based on the fact that organic compounds yield ions when burned in a flame. If two electrodes at a potential difference of about 150 volts are inserted in the flame, differences in conductivity can be measured as solutes are eluted from the chromatographic column and burned. The degree of ionization which occurs in the flame is much greater than would be predicted from the ionization potential of organic compounds. It has been suggested that this could be caused by the formation of carbon aggregates which are subsequently ionized readily due to the low work function of solid carbon. The detector is insensitive to temperature changes, vibrations, and small fluctuations in flow rates of carrier and flame gases. For hydrocarbons, response is roughly a function of carbon member, but rather large deviations from this are encountered from low molecular weight compounds containing functional groups. The detector does not respond to inorganic gases such as air, carbon dioxide, water vapor, ammonia, or hydrogen sulfide.

The dual flame ionization detector principle is the same as for a single flame. Using the two flames, one is charged with a negative potential of 150 - 180 volts and the other is charged positive. A single collector electrode is used so that only the net difference between the two is recorded on the meter. This arrangement automatically compensates for any bleeding from the reactant columns if the sample and reference side each has essentially the same compounds.

It was decided that a dual flame ionization detector would be desirable since the principle allows a compensation for any bleeding from the packing and reaction materials. The instrument has one flame tip charged positive and the other negative. The collector electrode is common giving only net signal. Although the idea seems simple enough, there are problems associated with the system. Perkin-Elmer Corporation marketed the first instrument and found that due to noise problems they were forced to redesign the instrument and replace all of the earlier models that had been marketed. A detector was ordered from Perkin-Elmer

for incorporation into the instrument and it was found that they could not deliver it in time for the completion of the project because of the problems they had encountered. The order was cancelled and a proto-type unit was obtained from Micro-Tek Instruments, Inc. This unit was also defective and Micro-Tek found that it was necessary to rede-sign it. The newly designed unit was obtained at the end of January and was later found to contain some flaws in the flow system.

An attempt was made to build a dual flame head in this laboratory and we had the same difficulties that had plagued Micro-Tek and Perkin-Elmer. No unit was available for laboratory work until after the Micro-Tek arrived in January and was installed in the final package. Provisions were made to permit the operation of the instrument on one flame if it became necessary or desirable. The screening of compounds was done on a Carad Flame Ionization Detector with a single flame.

C.   Development of the Reaction and Subtraction Tubes

The flame ionization detector required that all of the inorganic gases, to be measured, be converted to organic gases. This was neces-sary because the instrument does not respond to inorganics. Table 1 gives the composition of each of the tubes and the reaction for which it is used.

1.   HCl Detection

The reaction of HCl with silver acetylide to yield acetylene and silver chloride is a well known one. However, due to the sensitive nature of silver acetylide, it was decided to use the ethyl acetylene homo-log silver butylide (Ag Bu) hoping that it would give better response and would be safer to handle. The silver butylide can be prepared easily in the laboratory by passing ethyl acetylene through an ammoniacal silver solution. The silver butylide precipitates out and may be handled safely as long as it is wet. When the butylide dries it becomes very sensitive and dangerous to handle; thus it was decided to add a humectant in the form of glycerol. It was believed also that the reaction would go faster in the gas-liquid phase than in the gas-solid phase.

Silver propyl mercaptide was tested as a replacement for the silver butylide. However, it did not respond as well to HCl as the butylide and further work was suspended.

For the silver butylide to be specific for HCl, it was necessary to selectively subtract the HF which also reacts with the butylide. This was done by using "Dessicoted" glass beads.

TABLE 1

COMPOSITION OF REACTION/SUBTRACTION TUBES

Tubes		
	1-7	HF
	2-8	HCl
	3-9	NO_2
	4-10	O_3
	5-11	UDMH
	6-12	Blank

#1 AgNO$_3$/Glycerol   Ag Bu
        2.52g   0.59g

#2 Dessicote Beads   Ag Bu
        1.31g   0.58g

#3 Oleic Ac/FP 80   TBT 10%/FP 80
        0.89g   0.76g

#4 CrO$_3$/HgSO$_4$/   TBTO 10%/FP 80
    Silica Gel
        0.69g   0.71g

#5

#6 Blank

#7 AgNO$_3$/Glycerol - Dessicote - Ag Bu
        2.26g   1.29g   0.54g

#8 AgNO$_3$/Glycerol - Dessicote - Ag Bu
        2.32g   1.32g   0.61g

#9 Oleic Ac/FP 80 - CrO$_3$/HgSO$_4$ - TBT 10%/FP 80
        0.69g   0.64g   0.80g

#10 Oleic Ac/FP 80 - CrO$_3$/HgSO$_4$ - TBTO 10%/FP 80
        0.80g   0.55g   0.78g

#11

#12 Blank

To complete the HCl detection cycle it was necessary that the tubes going to the reference side of the dual flame should contain essentially the same components as the sample side. A tube containing silver butylide preceded by AgNO$_3$/glycerol and Dessicoted Beads for HCl and HF removal was used to compensate for any bleeding by the silver butylide.

2. HF Detection

The HF/silver butylide reaction is not as strong as the HCl/Ag-Bu reaction, but it is stronger than the HF/Tetrabutyl tin (TBT) reaction; therefore, it was decided to use the butylide. A short column of silver nitrate coated with glycerol was used to selectively remove the HCl from the stream.

The reference side of the HF cycle contained silver butylide preceded by AgNO$_3$/glycerol and Dessicoted Beads to compensate for bleeding and remove all HCl and HF.

3. Nitric Oxide Detection

It was found that NO$_2$ would react with tetrabutyl tin (TBT) to release a hydrocarbon, probably butene. At first the tetrabutyl tin was preceded by a tube of phosphoric acid coated onto potassium bromide. The NO$_2$ oxidized the KBr to Br$_2$ which in turn released butyl bromide from the organotin. However, it was later found that the conversion to Br$_2$ was not necessary and it was omitted.

The tetrabutyl tin is also oxidized by ozone so that it became necessary to remove the ozone on a column of oleic acid coated on Fluoro Pak 80 (FP 80) if the reaction was to be specific for NO$_2$.

The reference side of the NO$_2$ detection cycle consisted of a tube of TBT on FP 80 preceded by oleic acid on FP 80 and CrO$_3$/H$_2$SO$_4$/HgSO$_4$ on silica gel. This prevented any pollutants from reacting with the TBT and compensated for any bleeding by the TBT since presumably each side would bleed at the same rate.

4. Ozone Detection

It was found that ozone would oxidize bis (tributyl tin) oxide (TBTO) to give a hydrocarbon that could be measured in the flame. Since NO$_2$ also gives a reaction, it was subtracted on a column of chromic acid, sulfuric acid and mercuric sulfate on silica gel, to make the reaction specific for ozone.

The reference side of the O_3 cycle was a tube of TBTO on FP 80 preceded by oleic acid on FP 80 and $CrO_3/H_2SO_4/HgSO_4$ on silica gel. This prevented O_3 or NO_2 from reaching the TBTO and allowed a compensation for bleeding.

5. UDMH Detection

Since UDMH has two methyl groups attached, it was thought it could be determined directly in the flame ionization detector leaving only the necessity of subtracting it from the reference tube. Unfortunately this has proven to be most difficult. There are any number of reactions in the literature which will remove UDMH from a gas stream. These reactions all involve aldehydes that are too volatile for use with the flame ionization detector. There was some success with molecular sieve, however, it failed to remove the UDMH quantitatively.

There has not been a satisfactory method developed for the removal of UDMH; therefore, no method has been developed to detect the UDMH.

D. Optimization of the Reaction-Subtraction System

After the development of the chemical reaction and subtraction tubes, it was necessary to optimize them with regard to length, particle size and loading ratio. Included in this study was a test to assure that none of the pollutants were going through the reaction tubes unchanged. A system was devised where the sample from the pump was split in equal parts each about the normal flow to the detector; one side was passed through the reactant tube, the other through a blank. Then each side was collected and analyzed for the pollutant. It was found in each case that none of the gas passed through the reaction tube unreacted.

The optimization of the sample tube length and loading ratio was done by making reaction tube packings with loading ratios of 0.5%, 1.0%, 5% and 10%. The packing length was varied from 2.5 cm, 5.0 cm, 7.5 cm and 10.00 cm. The results of this study showed that 10% tetrabutyl tin or bis (tributyl tin) oxide on Fluoro Pak 80 gave the best results. It was applied with a hexane co-solvent. The optimum tube length proved to be five centimeters of reactant.

The silver butylide proved to be quite difficult to handle and there seems to be some batch to batch differences in sensitivity to HCl/HF. Due to the explosive nature of the material, it is not advisable to sieve to a uniform size; therefore, it must be used as is. It is, however, possible to break it into small particles (very carefully) while it is damp. Two explosions occurred during the tests. One was a quantity that had been

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dried completely and was stirred gently with a spatula. The second was a glass tube that was being filled; it is believed this one was set off by static electricity. No trouble was experienced with the silver butylide in the Teflon tubing. Glycerol was added as a humectant to desensitize the butylide.

The optimization of the subtraction tubes did not prove to be any problem other than adding enough material to insure all of the pollutant being removed from the stream.

E.   Air and Fuel Flow System

The air flow may be described as follows: Air enters the system through a small hole in the side of the case (when viewed looking at the control panel, the hole is on the left side) into the intake silencer, then into the compressor where the pressure is raised to about 40 in. H_2O, and finally passes through an outlet silencer. At this point, sweep air for the dual flame detector is taken from the main flow. The main flow continues to the selector valve assembly. The flow pattern through this assembly is as follows: Air enters a circular input manifold which has twelve outlets. Each outlet from this manifold has attached to it a 13-inch long piece of 1/8-inch I. D. teflon tubing. These tubes contain the analysis chemicals. Each tube is connected to a separate metering valve. The adjusting handles of these valves are marked with a number corresponding to the tube number. Clockwise rotation of any handle reduces the flow through that particular tube so that flow through all twelve tubes may be matched at any valve within the output capability of the compressor. Air flow from each metering valve then enters a separate 3-way, cam operated valve which either vents the metered flow into the instrument case or directs it into the appropriate outlet manifold. Tubes 1 through 6 are connected to the sample outlet manifold and tubes 7 through 12 are connected to the reference outlet manifold. The twelve 3-way valves are positioned radially in two banks of 6 each about a two lobe, solenoid actuated cam, such that in any cam position, air from one sample tube passes into the sample outlet manifold and only air from the one proper reference tube passes into the reference outlet manifold. All other tubes are vented into the case. The solenoid is actuated by a circuit which includes a microswitch that is closed and opened by the sprocket teeth which drive the chart of the recorder. Thus, the recorder becomes the timer for the entire sampling operation. The normal cycling rate is 2-1/2 minutes per position. A push-button, over-ride switch has been provided to enable the operator to cycle the system at any rate he chooses. Figure 1 is a schematic of the entire flow system.

Tubes are paired for operation as follows: 1 and 7, 2 and 8, 3 and 9, 4 and 10, 5 and 11, 6 and 12. Lights are provided on the control panel to indicate which pair of tubes is in operation.
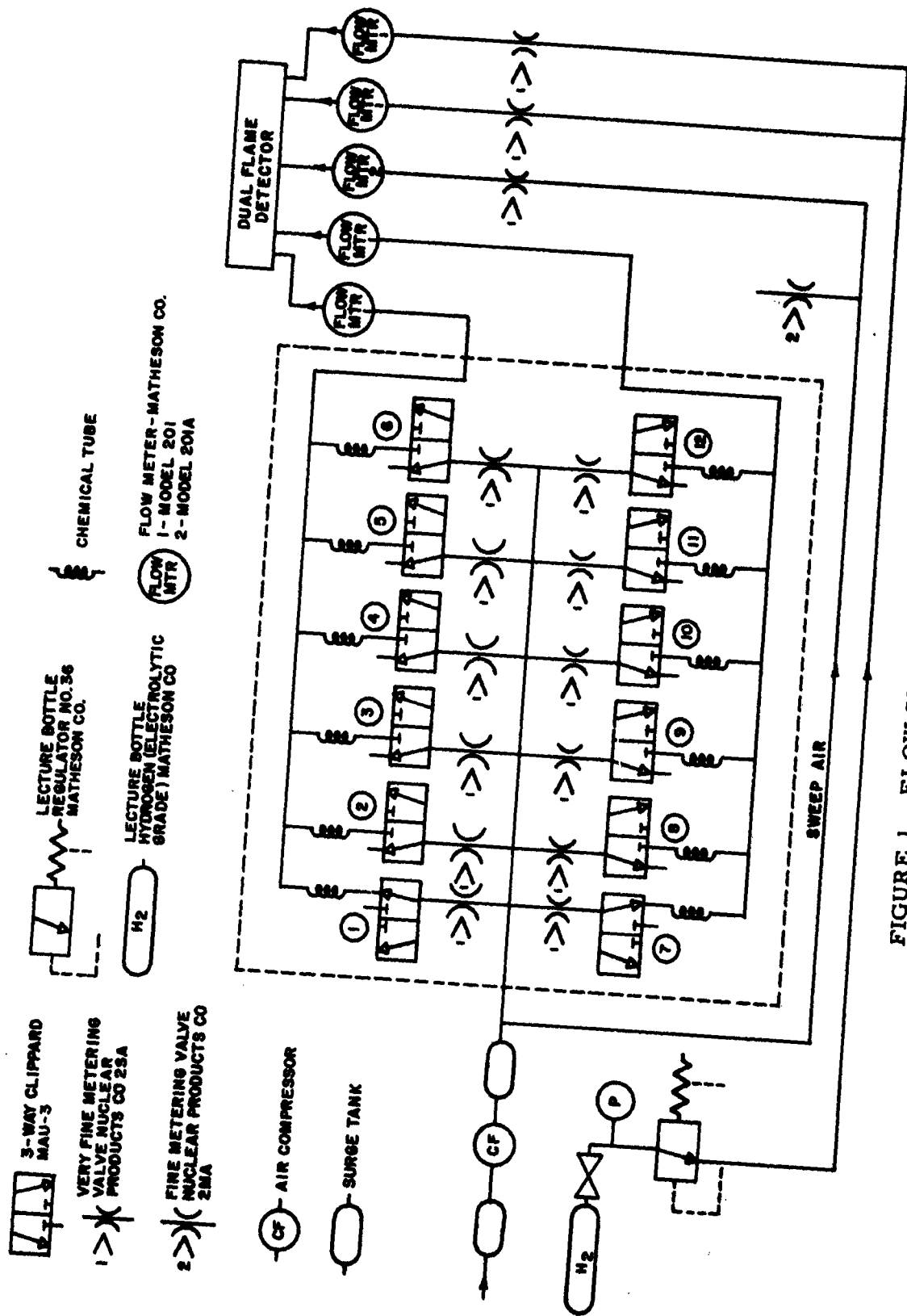
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FIGURE 1. FLOW SYSTEM SCHEMATIC

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Hydrogen is stored in a lecture bottle located at the bottom of the case, beneath the instrument panel. A shutoff valve (supplied as an integral part of the lecture bottle) is connected to a pressure regulator and then, through copper tubing, to the inlets of two metering valves located above the H_2 flowmeters. Flow is regulated by these metering valves. H_2 passes through flowmeters and into the two sides of the dual flame detector.

F.   Electronics

The instrument electronics is composed of the circuits and components required to furnish the operating power, detection, switching, and recording functions. The instrument is basically a differential flame ionization detector system with an electrometer amplifier and recorder. An integral pump supplies the sampled air to a sequentially selected, chemical reaction tube assembly. A block diagram is shown in Figure 2.

The primary operating power is derived from a nickel-cadmium battery packed with taps at 5, 12, and 24 volts. The diaphragm pump requires approximately 20 volts A. C. rms at a frequency of 60 cycles per second which is generated by the pump driver. The chemical reaction tubes are selected in sequence by a cam driven valve mechanism operated by a rotary stepping type actuator which also positions a rotary switch for indication of the selector position, and thus the gas to which the detector is sensitive. A dual flame detector is used to produce an electrical current output proportional to the magnitude of the differential trace gas present in the two sample streams. This small current is amplified by an electrometer and a differential amplifier to provide sufficient level to operate the meter movement of the recorder. The high D. C. positive and negative voltages required by the flame detector are furnished by the probe power supply. A selector circuit is used to provide timed relay contact closure which switches the rotary actuator in the desired sequence. Figure 3 is a schematic of the entire electronic system

1.   Electrometer

The electrometer circuit is of the balanced type with a single input. Type 5889 electrometer tubes are used as the input tubes followed by a Fairchild FSP-2 dual transistor connected as a differential emitter follower amplifier. The differential output from the emitter follower is further amplified in a Burr-Brown Type 1305 differential type operational amplifier which is connected to have a voltage gain of 10. The electrometer sensitivity is controlled by an externally mounted resistor-switch assembly which can connect a choice of either a 100,000 megohm or a 1,000,000 megohm resistor from the input terminal to ground.
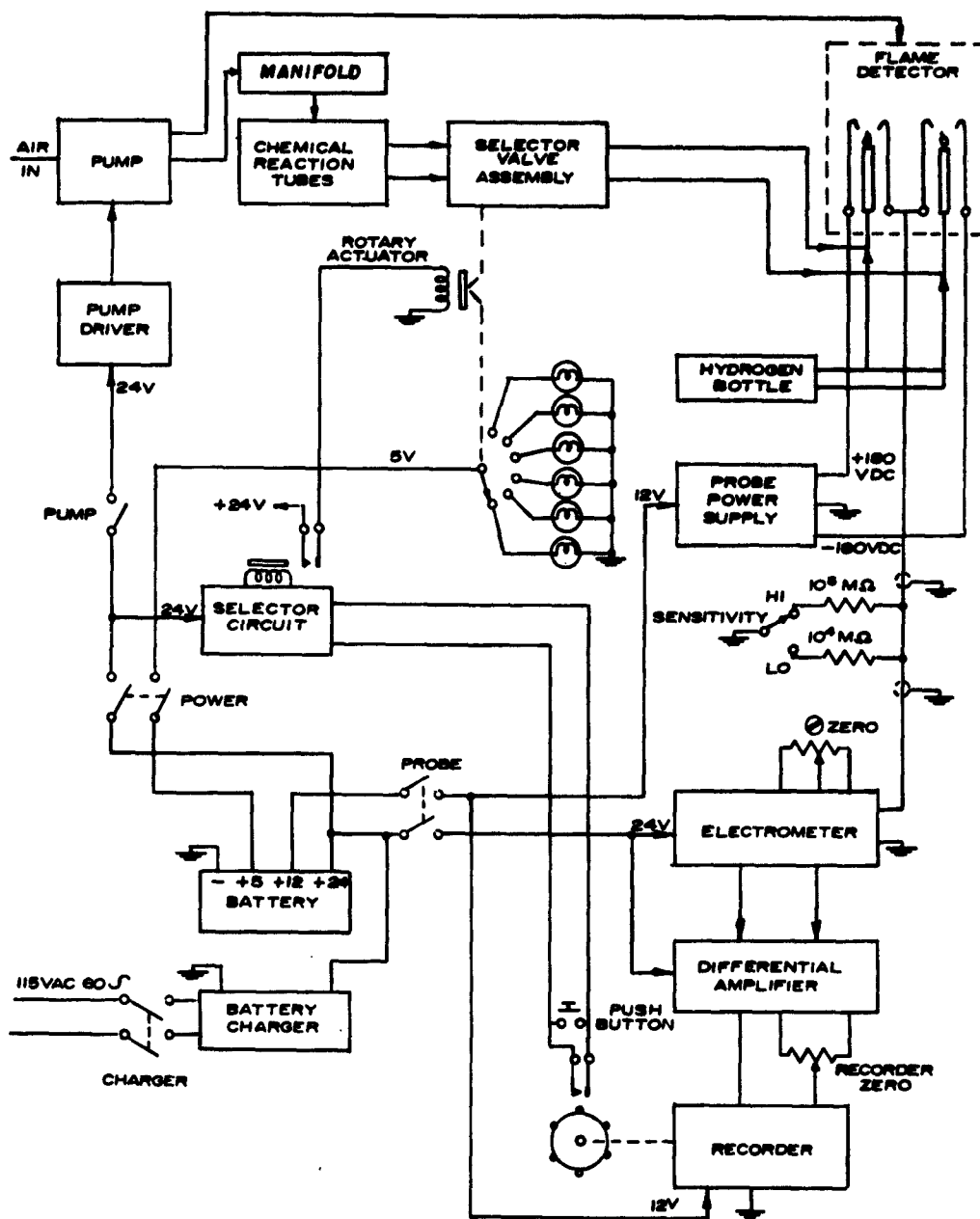
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FIGURE 2. BLOCK DIAGRAM

FIGURE 3. ELECTRONIC CIRCUIT DIAGRAM

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The 5889 is a very low leakage type electrometer tube rated for a maximum grid current of 3×10^{-15} amperes and was selected to provide an electrometer with a current sensitivity approaching 10^{-14} amperes. The balanced two-tube electrometer circuit is used to minimize drift due to environmental conditions and supply voltage variations. To further reduce effects of supply voltage variations, the plate supply potential is regulated at 13.5 volts by an IN3682 zener diode, and the filament source is regulated by an IN960A zener diode. The plate circuits of the electrometer tubes are connected to a balanced emitter follower amplifier using a single Fairchild FSP-2 transistor connected to provide near unity voltage gain and to transform the high plate impedance to a low value for connection to the following amplifier. The screen grids of the electrometer are connected through the FSP-2 transistor to provide improved stability. A screw driver adjustment "Trimpot," available through the top of the case, is connected to one screen grid to allow the electrometer circuit to be balanced. The adjustment is very critical and must be adjusted with care, only if proper equipment is available.

The differential output of the electrometer-emitter follower is amplified by a factor of 10 in a Burr-Brown Type 1305 operational amplifier with heavy negative feedback. This amplifier has a basic voltage gain of 20,000, and, by reducing the gain to 10 by use of negative feedback, very good stability is obtained. A "Trimpot" is available through the top of the shield can for zero setting of the 1305 amplifier, but the adjustment is very broad with the large negative feedback and should seldom, if ever, need adjusting.

The output of the 1305 amplifier is connected to one side of the recorder input. Since the output potential of the amplifier is normal about eight volts referenced to ground, the other recorder input is connected to a ten turn potentiometer across which is connected a total of 9.1 volts regulated by a zener diode. This ten turn potentiometer is adjusted to produce a net of zero volts across the recorder input terminals and is the normal zero adjustment control for the electrometer-amplifier-recorder.

The electrometer current sensitivity is controlled by shunting a resistor from the input terminal to ground. Two resistors for this purpose are mounted in a shielded enclosure, and the one to be used is selected by a toggle switch. In the high sensitivity position, the shunting resistor is 100,000 megohms, and, in the low sensitivity position, the resistor is 10,000 megohms. In the high sensitivity position, the current sensitivity is approximately 3×10^{-13} amperes for full scale recorder deflection, and, in the low sensitivity position, approximately 3×10^{-12} amperes is required for a full scale recorder deflection.

The sensitivity and stability are such that a short time current change of about 5×10^{-14} amperes can be detected.

The electrometer and emitter follower are constructed in a Burr-Brown case to match the 1305 amplifier. The 10-turn zero adjustment potentiometer, as well as the zener diodes and several resistors, is mounted in the base into which these assemblies are connected.

2.   Probe Power Supply

The probe power supply furnishes both a positive and a negative voltage referenced to ground to supply the potentials required by the probes in the dual flame ionization detector. These two potentials are about +180 volts and -180 volts and must be approximately equal for proper balance at the electrometer input. The two voltages may vary over the range of 160 to 200 volts, depending upon the state of charge in the battery power source, but will remain equal relative to each other.

The voltages are generated by a transistorized D. C. -D. C. convertor which steps up the 24 volt supply potential to the required value. The circuit uses a single 2N1302 transistor connected to one transformer in such a manner that nonsinusoidal oscillations are produced with a repetition rate of 500 to 1000 cps. The actual output waveform is a series of pulses with a duty cycle of about 10 to 1. These pulses on the transistor collector are stepped up in voltage by the two SP-4 transformers. The voltage on one secondary is rectified and filtered to produce the positive output while the voltage on the secondary of the other transformer is rectified and filtered to produce the negative output potential. The internal impedance of the supply is several hundred thousand ohms and any appreciable load current will cause the output voltage to be reduced. Measurement of the potential should only be attempted with a vacuum tube voltmeter if accurate results are to be obtained.

3.   Pump Driver

The pump driver furnishes 60-cycle A. C. power to operate the diaphragm type pump used in the air sampler. The pump used is of the resonant spring-mass type which must be driven on its resonant frequency for best efficiency and capacity. Since the pump was originally designed for 115-volt, 60-cps operation, it is necessary that 60-cps A. C. power be used for operating this component. The original pump coil was rewound with larger wire and fewer turns to make the voltage requirements more compatible with voltages which could be obtained directly from transistors operating on the 24-volts D. C. potential of the battery

pack   The voltage requirement for the pump is now about 20 volts rms at the same 60-cycle frequency.

The pump driver is composed of a 60-cycle oscillator, followed by an emitter follower amplifier which supplies the required drive to a push-pull power amplifier which is directly connected to the pump coil.   The oscillator uses a UTC 0-9 transformer winding, tuned by a capacitance of 0.375 microfarad to resonate at 60 cps.   The secondary winding on this same transformer is connected to provide the necessary feedback for oscillation   A 2N696 transistor furnished the amplification for the oscillator to function.   The output from the oscillator is a very clean sine wave.   A 2N1038 transistor is used as an emitter follower to provide a high input impedance for connection to the oscillator output and to furnish the necessary power amplification to drive the push-pull power amplifier.   The power amplifier uses two Type 2N301 power transistors which are transformer coupled to the 2N1038 emitter follower.   The collectors of the 2N301 transistors are each connected to opposite ends of the pump coil, and the pump coil center tap is grounded.   The capacitors connected from collector to collector of the 2N301's and across the pump coil are used to resonate the coil to 60 cps and greatly improve the circuit efficiency and output capability. The output voltage across the pump is a slightly distorted sine wave.

Every effort was made to minimize the power consumption of the pump driver since this is the most power-consuming circuit in the instrument due to the relatively large amount of continuous work performed by the pump in compressing the large volume of air required. The total current drain for this final design is about 0.65 amperes.

4.   Selector Circuit

The selector circuit provides relay contact closures of the proper length of time and at the proper time interval to sequentially advance the rotary actuator used to select the set of chemical reaction tubes to be used.   The rotary actuator requires a current of about 3.5 amperes at 24 volts D. C. to advance the selector valve assembly one position.   Since it is necessary for low average power consumption to minimize the time during which this heavy load is across the batteries, the selector circuit relay closes the circuit to the rotary actuator for the minimum amount of time necessary for reliable operation.   This closure time is on the order of 0.2 seconds.   The chemical reaction times are such that a 2.5-minute time on each set of tubes is satisfactory. The selector circuit thus provides the above short relay contact closure time at intervals of 2.5 minutes.

Since an accurately regulated shaft speed was available on the chart recorder, this was used to operate a switch to provide the required selector time intervals. A multi-projection cam which was originally intended to pull the chart paper through perforated holes was available on the recorder chart drive shaft. A microswitch was mounted on the recorder in such a manner that these projections on the chart drive wheel caused it to be closed as each projection passed by the switch lever. Since the desired time intervals for advancing the reaction selector was twice the time for the spacing between these chart drive wheel projections, an electronic circuit was incorporated in the instrument for selecting alternate closures of the microswitch for advancing the reaction selector mechanism.

The microswitch closure applied a fast rise time D. C. potential to the input of the selector circuit. This input signal is differentiated and applied as a short pulse to a flip-flop circuit. The flip-flop is set in one state by the first input pulse but does not generate an output signal. The signal input pulse causes the flip-flop to be reset to the original condition and generates an output pulse to the input of a one shot (monostable) multivibrator circuit. The one shot circuit causes a relay to be energized for a length of time set by the circuit time constant. The contacts on this relay are used to energize the rotary acuator solenoid and advance the chemical reaction cam operated valve mechanism to the next position. The result of this circuit is that the first microswitch closure does not cause the relay to be energized but sets the flip-flop so that the next microswitch closure causes the relay contacts to close for about 0.2 seconds.

A push button mounted on the control panel is wired in parallel with the microswitch. Closing this push button causes the same action as the microswitch closures and advances the selector mechanism one step on alternate switch closures. If the microswitch contacts are in a closed condition, which occurs about 20% of the time, operating the front panel push button will have no effect since the circuit is already closed by the microswitch contacts.

A rotary switch mounted on the rotary actuator shaft is used to select one of six miniature 5-volt lights mounted on the front panel. These lights indicate the position of the selector mechanism.

5.   Battery and Charger

The primary power source for the instrument is two 15-ampere hour nickel-cadmium batteries. Each battery is composed of ten cells and has a nominal output potential of 12 to 13.5 volts, depending on the state of charge. The batteries are connected in series to

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provide a total potential of 24 to 27 volts. Taps are provided to produce outputs of nominally 5, 12, and 24 volts.

The battery capacity and weight are determined by the length of operating time required. Since the total current required to operate the complete instrument is about 0.8 amperes, the 15-ampere-hour battery mounted in the instrument should allow operation for a period of about 19 hours without recharging, provided the battery is fully charged prior to the start of operation. Since the major portion of the instrument weight is that of the battery, a considerable weight reduction could be achieved by replacing the 15-ampere-hour battery by one of smaller capacity if operation for shorter time periods is sufficient.

A circuit is incorporated in the instrument for recharging the battery from a 115-volt 60-cycle power line. The charger is turned on by a panel mounted switch which controls the 115-volt A. C. power to a transformer primary. The transformer steps down the input voltage to 24 volts rms. This voltage is rectified by a bridge rectifier composed of four Diodes, Inc. Type DI-54 diodes. The output of the bridge is used to charge the battery. The charging current is limited by a Type 82 lamp which acts as a variable resistance. The nominal charging current is about 1 ampere which makes a charging time of about 18 hours necessary for fully recharging a completely discharged battery. The maximum charger output potential is chosen to be nearly equal to the fully charged battery potential and there is little danger of damage due to overcharging; however, when the battery reaches a near fully charged state, it begins to bubble excessively and may cause some leakage of electrolyte which could attack the aluminum frame and cause some damage. For this reason, if the battery is to be left on the charger for very long periods in excess of that required to recharge, it is advisable to remove the battery from the case and leave it during the charge. The interconnecting cables are sufficiently long to permit electrical connection with the battery a foot or so outside the case. The instrument may be operated with the charger turned on and the battery being recharged. If the instrument is turned on, the charger turned on, and the battery disconnected, the regulator lamp can be burned out.

6.   Recorder

The basic recorder used in the instrument is an Amprobe Type DC500 miniature 3-inch chart width unit. The recorder uses a standard meter movement to actuate the recording stylus; has a sensitivity of 500-D. C. microamperes for full scale deflection; and has a chart speed of 12 inch per hour. The standard roll of chart paper is 30 feet long which permits 30 hours of continuous recording with one roll. The recording is achieved by periodically pressing a stylus

mounted on the end of the meter indicator against the pressure sensitive paper. The resultant record is not absolutely continuous, but, since the stylus is pressed against the paper at intervals of once every 5 seconds, there is a sufficient number of points to make a line that is sufficiently continuous for most purposes. The number of reading points for each half inch of recording (the chart length for 2-1/2 minutes--the length of each sampling period) is 30.

The recorder originally was supplied with a 115-volt 60-cps motor. To minimize the power drain, this motor was replaced with an A. W. Haydon Type K-5630-P2 chronometrically governed 12-volt D. C. motor. The motor speed is 12 rpm.

The recorder was further modified to mount the micro-switch required by the selector circuit. The microswitch is mounted on the rear of the recorder in such a manner that the chart drive wheel projections cause it to be closed once for each 1/4 inch of chart paper movement. The chemical selector switching is thus synchronized with the chart recorder.

By removing the chart paper, the recorder meter may be used as a conventional panel meter for indication of the electrometer output. A thumb operated rotary switch on the side of the recorder allows selection of either record, meter, or off modes of operation. The switch must be in the record position for the chart to be driven even though the drive motor runs in other positions.

III. RESULTS AND CONCLUSIONS

The results obtained from the instrument have not been satisfactory because the dual flame has not functioned properly. The dual flame detector presently on the instrument is the third detector that has been used. The first detector did not function because the sweep air flow inadvertantly resulted in venturi effects giving a high noise level. The second detector proved to have uneven pressure drops across the two flame tips and was replaced. The third detector leaked voltage across the ceramic insulators with a net result that the probes did not get equal voltages. The voltage varied greatly and intermittently. The ceramic insulators were replaced with Teflon insulators. It was discovered also that the collector electrode was shorted in the body of the detector. After repair the instrument seemed to be much more sensitive than before.

In view of the difficulties experienced with the dual flame detector, it is concluded that much more extensive work is needed on the instrument before it would be acceptable for other than laboratory use. It should be pointed out that all of the major instrument manufacturers are still having trouble with the dual flame.

The response of the conversion tubes is in the desired range. It is believed that much better yields can be obtained through the development of better reactants. The original investigations, of course, were made with the Carad Flame Ionization Detector which is a single flame unit. The results of the tests can be seen in Figure 4.
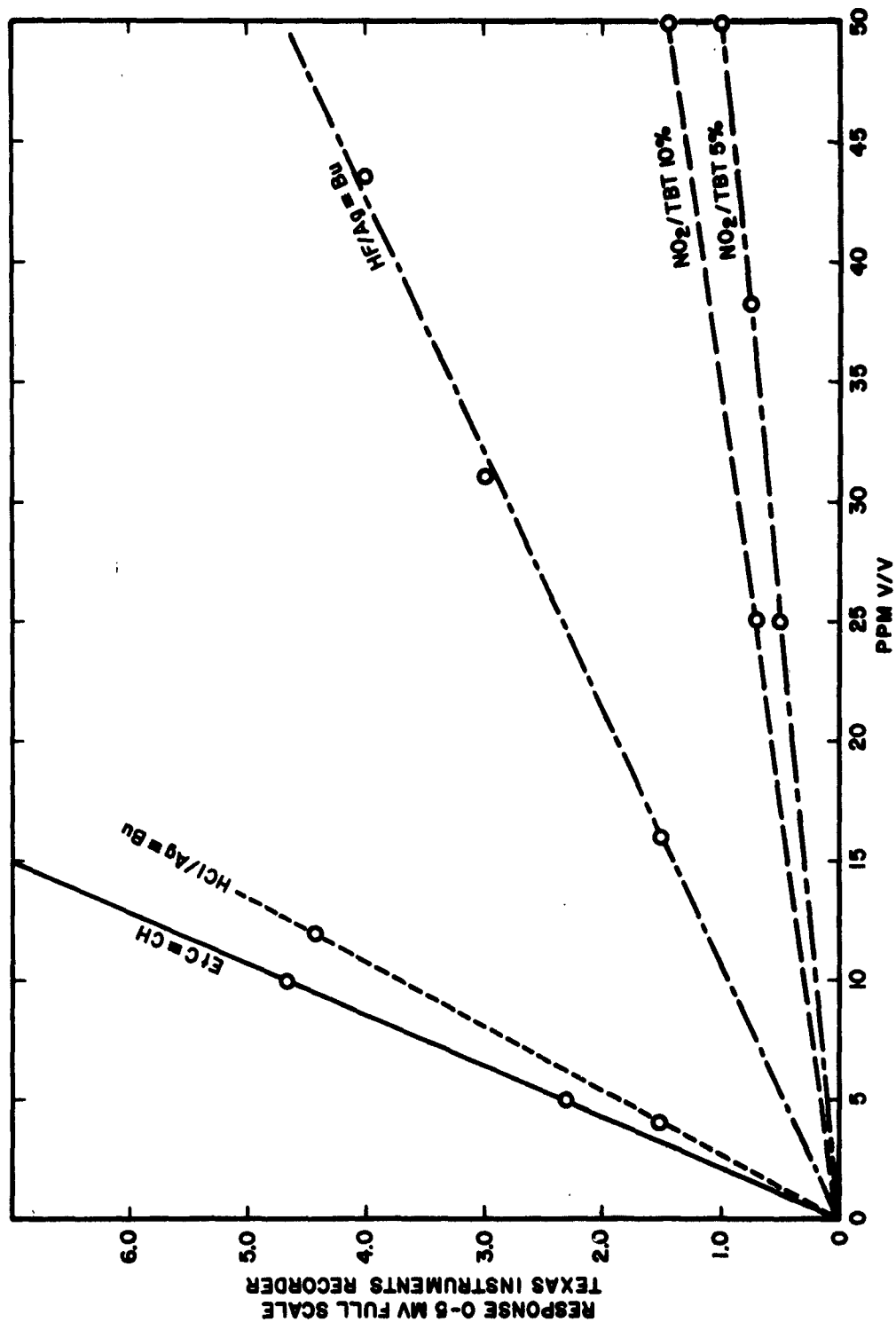
FIGURE 4. SAMPLES RUN ON ON CARAD .03X SCALE
H₂ FLOW .04 cfh
SAMPLE FLOW .04 cfh

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IV. RECOMMENDATIONS FOR FUTURE WORK

The present device can be improved upon in several ways. There is a large number of organo-metallic compounds that can be explored. It is quite feasible that some of these would improve the sensitivity of the instrument. The investigation of new reactants should be made if the existing dual flame system is to be used. These would include compounds of the Grignard class, some of the other organo-tins, and clathrates.

The idea of using radioactive tracers looks particularly enticing. The existing sample system would be used in connection with a radioactive tracer detector. The majority of the work would be done using flame ionization detectors until the optimum reactants had been found. Then, a synthesis program would be necessary to prepare the reactants using Carbon 14. The pollutants then would release the C^{14} labeled hydrocarbons from the reaction tube and would be measured using radioactive tracer techniques. The advantages of this procedure is the elimination of the need for a hydrogen source and the use of the dual flame ionization detector which is really not a proven instrument as yet.

Another possibility is the use of a standard laboratory gas chromatograph serviced by several sampling devices. The sampling device would consist of the present sample valve selector and reaction-subtraction tubes. The hydrocarbons released by the pollutants would be collected in a freezeout trap (salt and ice) and then separated and measured on the chromatograph at a later time. This would reduce the size and weight of the sample collection apparatus and would allow the collection of samples at several locations simultaneously with a minimum outlay of equipment. In the event this procedure were followed, it would still be desirable to improve on the materials used in the reaction tubes. It is not felt that the best possible reactants have been obtained due to a lack of time for exploration.

It is recommended that a different pump be used as the one in the system has been found to be marginal in its flows due to the pressure drop within the flow system.

In view of the difficulties that have been experienced with the dual flame ionization detector and inasmuch as it is as yet not completely proven, it is felt that a different type detector should be used in future work.

V. OPERATING INSTRUCTIONS

A. Instrument Power Supply

1. Check battery leads - Battery leads must be connected (Red/Red).

2. Plug battery charger lead into 110V. A. C. line - Turn on switch marked "Charger".

3. If the battery is in a discharged condition, do not try to operate unit until battery is recharged. The charger will not operate unit alone.

4. Charge up time for completely discharged battery is about fifteen hours. The light becomes dim when the battery is recharged.

5. Battery life is about 15 hours. When possible, it is recommended that the instrument be used with charger on.

B. Startup Procedure

1. Turn on switch marked "Pump".

2. Turn on hydrogen flow by turning lecture bottle to the left or counter clockwise.

3. Adjust hydrogen flow using needle valves and observing flow on flow meter. Adjust to .04 cfh. Once adjusted properly it should not require changing.

4. Turn recorder to "M" position; remove chart paper to expose meter. Chart paper can be removed by lifting the bright plate cover on recorder.

5. Turn on switch marked "Probe".

6. After hydrogen has been flowing for three minutes, remove the cover on the detector head by lifting the knob and insert a lighted pipe cleaner to ignite the detector. The pipe cleaner works better if first saturated with alcohol or lighter fluid.

7. Allow the instrument to equilibrate for a few minutes; then use the cam selector to advance to the desired sampling position by pressing the red button on the right of the indicator lights. Set the selector on position six initially, this indicates the zero base line. Use zero adjust knob on lower right corner to adjust zero.

8. Replace paper in recorder and turn recorder switch to "Record" and mark first recorder point on chart.

9. Each subsequent selector position then utilizes two lines on the chart paper, and these can be utilized to keep track of the positions for later analysis of data.

10. The indicated positions refer to the sampling of the pollutants as follows:

Position 1. HF
2. HCl
3. NO_2
4. O_3
5. Blank
6. Zero Base

C. Air and Hydrogen Flow Adjustment

Due to the construction of the dual flame detector, it is necessary that the air and hydrogen flows be regulated simultaneously. As seen in Figure 1, the task is that of regulating two parallel 2-component systems. Each system is composed of a flow of hydrogen and a flow of air. The air flow is selected from one of six chemical tubes for each system.

1. Remove the batteries. There are three screws holding the batteries in place, one at each lower corner and one at the upper left corner (viewed from the back of the case). Disconnect the cable and lean the battery forward to remove it from the case.

2. Remove the selector valve assembly from the instrument case. The selector valve assembly is the cylindrical aluminum can standing on end in the left rear corner of the instrument case. Disconnect the three air lines at the top of the case, unplug both electrical cables toward the bottom of the case and unscrew the band clamp which holds the assembly in position.

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It will be noted that the tubes at the top of the case are color coded. The center tube, which is the input from the compressor, is uncoded and fits only the center connection. The rear tube (coded red) is the output tube from the sample output manifold (1-6). The other tube (coded yellow) is the output tube from the reference output manifold (7-12). Remove the bottom cover from the selector assembly (the bottom is the end opposite the three tubes). With the bottom cover removed, there are 12 metering valve handles exposed. Each of these handles has a number corresponding to the chemical tube whose flow it controls.

3. Using the three tygon extension tubes provided in the repair kit, reconnect the selector valve assembly to the instrument. Connect the batteries. Be certain that color coding is observed in both tubing and cable connections.

4. Open the hydrogen valve attached to the lecture bottle, and set the hydrogen flow on each side of the detector to .04 CFH on the flow meter using the needle valves above the flow meters.

Next, start the compressor and set the sweep air at .5 CFH. The sweep air metering valve is located directly above the center flow meter. The valve to the right of the sweep air metering valve is provided to bleed off excess air, should such become necessary. Normally, the excess air bleed valve should be closed.

5. Push the "Advance" button (located on the front panel) until the position One is indicated. With the selector valve in position One, adjust metering valve No. 1 such that the flow is .04 CFH and metering valve No. 7 so that the flow is .04 CFH. Repeat for each sample position adjusting each pair. Correct the hydrogen and sweep air flows and repeat the selector meter valve adjustments. It is necessary to repeat this adjustment sequence about three times.

6. When the adjustment has been completed to satisfaction, reassemble in the reverse order. Care must be taken that the selector valve case does not touch the compressor. Such contact is evidenced by increased compressor noise and decreased flow capability.

CHEMICAL TUBE REPLACEMENT

Remove the selector valve assembly from the instrument case as described in the section on Flow Adjustment (1) and (2). Next, remove the two binding head screws which clamp the bracket containing the three tube connectors to the top cover of the selector valve assembly. (Remove the six screws holding the top cover to the band just below the center of the assembly). Remove the tubular plastic cover by unsnapping the lower edges.

The input manifold, chemical tubes, metering valves, 3-way valves, and two output manifolds are exposed. It should be noted that the chemical tubes are numbered and are connected to correspondingly numbered outlets from the circular input manifold and inlets to the proper metering valves.

Remove the chemical tubes by pulling them off the metal tubes which have been inserted in their ends. When installing new tubes, make certain that they connect to the properly numbered inlet and outlet and that the outlet end of the tube (the end with the numbered label) is attached to the inlet to the metering valve.

Reassemble the unit in the reverse order and perform the flow adjustment sequence.

VI. PREPARATION OF COLUMNS

A. Silver Nitrate/Glycerol

The silver nitrate is crushed with a mortar and pestle until the particle size is approximately 60-80 mesh; then glycerol is added carefully until the surface of the silver nitrate is coated. Care should be taken that too much glycerol is not added so as to make it difficult to handle.

B. Silver Butylide

The silver butylide is prepared by passing 1-butyne (ethyl acetylene) through an ammoniacal solution of silver oxide. A yellow precipitate is formed. This precipitate is then filtered out, washed free of ammonia with distilled water, usually about three washings with the last washing containing 10% glycerol. Silver butylide is dried in an evaporating dish in a hood preferably. While the butylide is still damp, it is carefully removed from the surface of the filter paper, and the larger particles are broken into the size that is desired. It is recommended that this material not be sieved. It is too sensitive. It is also recommended that a safety shield be used while handling silver butylide. The ethyl acetylene is available from the Matheson Co.

C. Dessicoted Beads

A good supply of Dessicoted beads has been furnished; however, if it is necessary to prepare more, the Dessicote is available from Beckman Instruments, Inc. The glass beads should be surface dried but not heat dried and dropped into a 10:90 mixture of Dessicote and acetone. The acetone is then driven off and the beads are coated.

D. Oleic Acid - Fluoro-Pak 80

A quantity of Fluoro-Pak 80 which is a mealy fluorocarbon polymer is weighed out. Then 10% by weight oleic acid is added to the Fluoro-Pak. Complete coating is achieved through the use of a co-solvent which serves to dilute the oleic acid and wet the surface of the Fluoro-Pak 80. Methanol or ethanol have been used with good success as a co-solvent. The mixture should be stirred constantly while heating gently over a hot plate until all of the solvent has been driven off. The Fluoro-Pak 80 is available from W. H. Curtin Co. Chemical Supply House.

E.   10% Tetrabutyl Tin on Fluoro-Pak 80

The fluoro-Pak 80 is weighed out and 10% tetrabutyl tin by weight is added to the Fluoro-Pak 80. The best co-solvent for this system appears to be hexane. The hexane is added, stirred carefully while heating over a hot plate to drive off the solvent.

F.   10% Bis (Tributyl Tin) Oxide on Fluoro-Pak 80

The bis (tributyl tin) oxide on Fluoro-Pak 80 is prepared by weighing out a quantity of Fluoro-Pak 80 and adding 10% bis (tributyl tin) oxide and stirring well, mixing well without a solvent. There does not appear to be a suitable solvent for bis (tributyl tin) oxide. The mixture should be stirred until a fairly even coating is obtained on the surface of all the Fluoro-Pak 80. The bis (tributyl tin) oxide is available from Metal and Thermite Corporation, Woodbridge Ave., Rahway, New Jersey.

G. CrO_3/$HgSO_4$/H_2SO_4 on Silica Gel

This reagent is prepared by making a 50-50 mixture of the CrO_3 and $HgSO_4$, dissolving it in a minimum amount of sulfuric acid and adding silica gel 200 mesh until the silica gel absorbs all of the mixture and becomes almost free flowing.

RADC, Research and Technology Division,
Air Force Systems Command, USAF,
Griffiss Air Force Base, New York.
Rpt Nr RADC-TDR-63-176. DEVELOP-
MENT OF A DEVICE TO OBJECTIVELY
DETECT AND RECORD THE PRESENCE
OF MINUTE AMOUNTS OF GASES IN THE
ATMOSPHERE. Final Report, March 13,
1963, 30p. incl illus, tables.

Unclassified Report

An electro-chemical sensing device has
been developed for the measurement of
HCl, HF, NO_2, and O_3. The instrument

has a dual flame ionization detector that
can also be operated as a single flame.
The inorganic gases are converted to
organic gases which are then detected
with the flame ionization detector.

I.   AFSC Project 5534,
      Task 553402
II.   Contract AF 30
      (602)-2655
III. Southwest Research
      Institute, San
      Antonio, Texas
IV.   H. P. Burchfield,
      et al.
V.   In ASTIA collection
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